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Pteropods from the Caribbean Sea: variations in calcification as an indicator of past ocean carbonate saturation

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Abstract. The aragonite shell-bearing thecosome pteropods are an important component of the oceanic plankton. However, with increasing pCO_2 and the associated reduction in oceanic pH (ocean acidification), thecosome pteropods are thought to be particularly vulnerable to shell dissolution. The distribution and preservation of pteropods over the last 250 000 years have been investigated in marine sediment cores from the Caribbean Sea close to the island of Montserrat. Using the *Limacina* Dissolution Index (LDX), fluctuations in pteropod calcification through the most recent glacial/interglacial cycles are documented. By comparison to the oxygen isotope record (global ice volume), we show that pteropod calcification is closely linked to global changes in pCO_2 and pH and is, therefore, a global signal. These data are in agreement with the findings of experiments upon living pteropods, which show that variations in pH can greatly affect aragonitic shells. The results of this study provide information which may be useful in the prediction of future changes to the pteropod assemblage caused by ocean acidification.

1 Introduction

The faunal responses to ocean acidification (the reduced availability of carbonate ions) are still largely unknown, although experimental evidence reveals that a reduction in pH typically leads to a decrease in calcification rates of a number of, but not all organisms (Feely et al., 2004; Orr et al., 2005; Guinotte and Fabry, 2008; Turley et al., 2010). To date, little information is available about important planktic producers of calcium carbonate. Several studies have investigated coccolithophore and planktic foraminiferal responses, but only three species of the aragonite-producing thecosome pteropods have been considered (Fabry et al., 2008; Comeau et al., 2009, 2010a, b). Here we demonstrate a relationship between the calcification of pteropod shells and past atmospheric CO_2 concentrations through the last 250 000 years by using low resolution Vostok CO_2 data and the high resolution oxygen isotope record. A diverse and abundant assemblage of pteropods and heteropods is recorded from marine cores collected from the Caribbean Sea offshore Montserrat. A number of these cores contain intervals of well-preserved pteropods which are associated with the glacial periods of the Late Pleistocene (Messenger et al., 2010). These well-preserved levels appear to be of widespread significance and a response to global climate change.

The group of holoplanktic molluscs known as the Pteropoda consists of two orders; the shell-less gymnosomes and the shell-bearing thecosomes (Fig. 1). These two orders are now considered to be less closely related than originally thought, but the term "pteropod" is still widely used (van der Spoel, 1976; Bé and Gilmer, 1977; Lalli and Gilmer, 1989). Thecosome pteropods are a common component of the water column throughout the world's oceans and can reach densities of up to 10 000 individuals per cubic metre (The Royal Society, 2005; Fabry et al., 2008). They are consequently important prey to a number of large cetaceans and commercial fish (The Royal Society, 2005). This study focuses on the species *Limacina inflata*, a common euthecosome (suborder of thecosomata) pteropod.

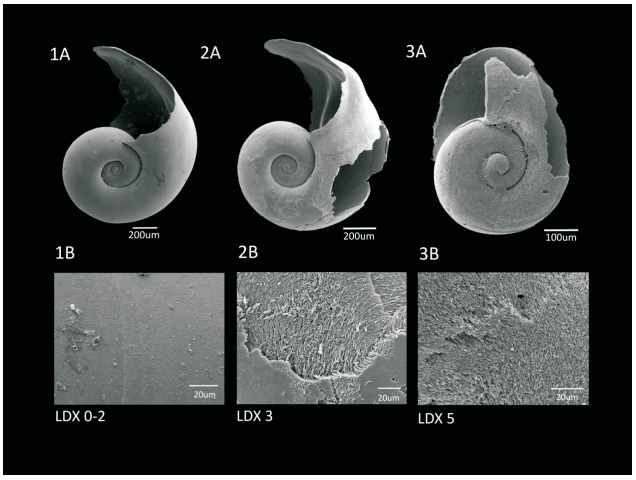

Fig. 1. Thecosome pteropod *Limacina inflata* from the Caribbean Sea near Montserrat at different stages of shell calcification.

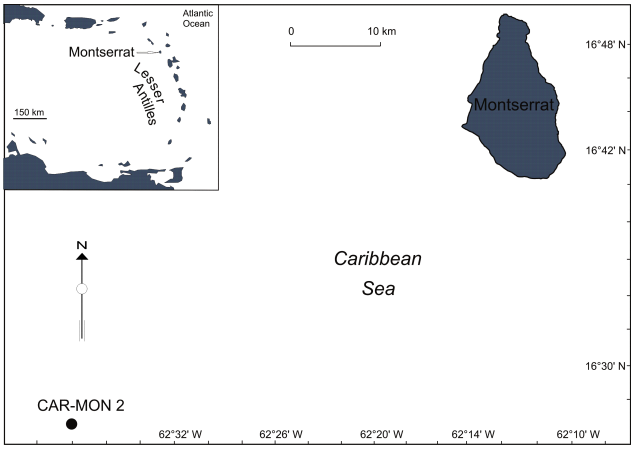

Fig. 2. Map of the Lesser Antilles showing the island of Montserrat and the location of core CAR–MON 2. A full bathymetric map of the area is available in Le Friant et al. (2004).

All euthecosome pteropods produce calcareous shells from aragonite, a polymorph of calcium carbonate, which is particularly susceptible to dissolution (50 % more susceptible than calcite): see Mucci (1983), Millero (1996), Morse and Arvidson (2002) and Klöcker et al. (2006). This makes their shells extremely vulnerable to the effects of ocean acidification, making it more difficult for them to grow and maintain their shells. It also means that, upon death, their shells frequently dissolve as they settle through the water column to the sea floor. This limits their occurrence in sediments to water depths of less than 3000 m and also restricts their presence in the geological record (Curry, 1971; Herman, 1971; Berner, 1977). The distribution of the modern fauna is well known (Bé and Gilmer, 1977) and "pteropod oozes" have been recognised for over one hundred years (Murray and Renard, 1891). With current increasing levels of atmospheric CO_2 and the resulting ocean acidification (Orr et al., 2005; The Royal Society, 2005), pteropods with their aragonitic shells are the subject of renewed interest, since they are likely to be the most vulnerable of the major planktic producers of $CaCO_3$. They are also likely to be the first planktic fauna to experience persistent decreased $CaCO_3$ saturation states. As an important part of the food web, especially in the Arctic and Southern Oceans, their potential demise is of great significance.

2 Marine sediment cores from Montserrat

In March 2002, as part of a multi-disciplinary project on the volcanic activity on the island of Montserrat, the R/V *L'Atalante* recovered a series of piston-cores from the ocean floor surrounding the island (Fig. 2). Of the 12 cores collected on the "Caraval Cruise", CAR-MON 2 provides the longest time record (Le Friant et al., 2008 document in detail the collection techniques and subsequent methodologies employed). The site of CAR-MON 2, in 1102 m of water, is located at 16°27.699′N, 62°38.077′W. The oxygen isotope (δ^{18}O) profile of CAR-MON 2 (Fig. 3) gives an accurate record of the Marine Isotope Stages (MIS) back ∼250 000 years BP and the record compares well with other studies (Imbrie et al., 1984; Prell et al., 1986). This δ^{18}O profile has been verified using a limited number of AMS radiocarbon dates and ^{39}Ar/^{40}Ar radiometric dates (Le Friant et al., 2008). Using the >150 µm size fraction, counts of the planktic foraminifera have allowed the determination of the *Globorotalia menardii* zonation (Ericson and Wollin, 1956; Reid et al., 1996; Le Friant et al., 2008).

Reduced calcification of *Limacina inflata* shells has been quantified throughout CAR-MON 2 using the scale published by Gerhardt and Henrich (2001). As the *Limacina* Dissolution Index (LDX) has only been used by a limited number of workers (e.g., Klöcker et al., 2006) on "fossil" material, its calculation is now described.

Pre-processed and dried sediment (Le Friant et al., 2008) was used to collect just over 300 (or as many as were present) pteropod specimens from two size fractions (>500 µm and 150–500 µm) at varying intervals. Only whole specimens that retained their protoconch and protoconch fragments were counted. Determination of the calcification of the pteropod shells was made using the *Limacina* Dissolution Index (LDX) which was devised by Gerhardt et al. (2000) and published as a scale by Gerhardt and Henrich (2001). This method involves the semi-quantitative analysis of the surface of the pteropod shell on a scale of 0 to 5; 0 being a pristine, transparent, lustrous shell with a smooth surface and 5 being an opaque, white and completely lustreless shell with additional damage. At least 10 shells (max 30 shells) of adult *Limacina inflata* of a size of 300 µm or larger were allocated a value from this scale by the use of light microscopy for each

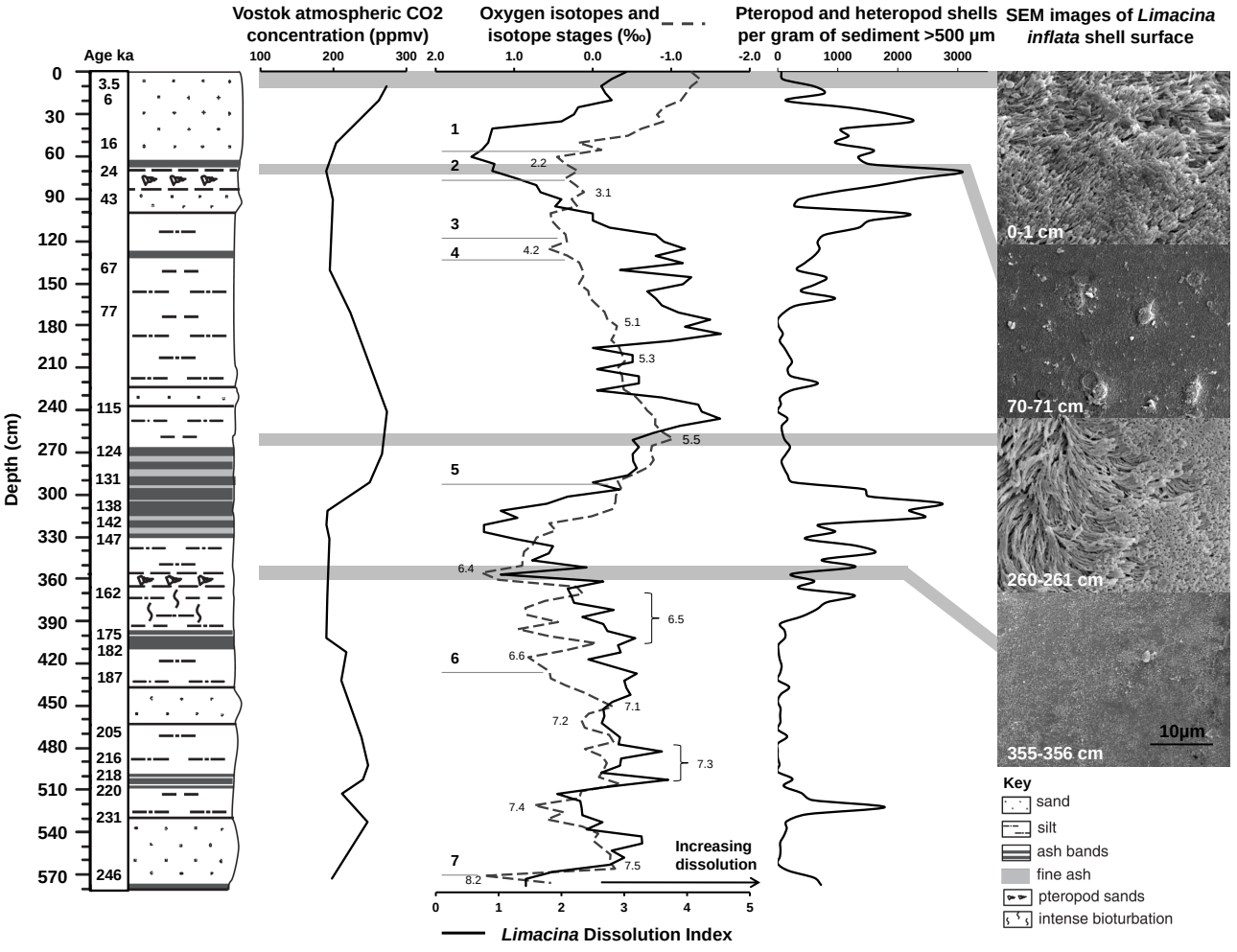

Fig. 3. Sedimentary log for core CAR–MON 2 including age model (from oxygen isotope stratigraphy) from Le Friant et al. (2008), Vostok atmospheric CO_2 concentrations, stable isotope stratigraphy (Marine Isotope Stages), pteropod calcification (LDX) and abundance of >500 µm pteropod and heteropod shells: partly modified after Le Friant et al. (2008).

sample. The average for each sample was then calculated to provide the LDX value.

3 Pteropod calcification record

CAR-MON 2 records three levels of particularly well preserved, abundant and diverse pteropods (Fig. 3), two of which have been documented previously (Le Friant et al., 2008; Messenger et al., 2010) but not studied in detail. The upper concentration of pteropods is found in MIS 2 and has been dated at around 25 000 years BP (55–80 cm), with a peak in pteropod preservation at MIS 2.2 (∼20 000 years BP). The middle concentration of pteropods is within MIS 6 (295–425 cm) with a peak in preservation at MIS 6.4, dated at about 150 000 years BP and the lower concentration is found within MIS 8 at the very base of the core (565–575 cm), with a peak in preservation at MIS 8.2. The upper concentration of pteropods corresponds almost exactly with the "pteropod sands" reported by Chen (1968) from the Gulf of Mexico, Venezuela Basin and other occurrences in the Caribbean Sea, Mediterranean Sea and Red Sea. Chen (1968) suggests that their widespread occurrence was controlled by Late Pleistocene climate changes.

This latest Pleistocene occurrence of abundant pteropods has also been recorded in the Andaman Sea (Sijinkumar et al., 2010), in the Red Sea (Almogi-Labin et al., 1991), off-shore Florida (Gardulski et al., 1990), on the western flank of the Great Bahama Bank (Eberli et al., 1997; Messenger et al., 2010), on the Brazilian Slope (Gerhardt et al., 2000), in the Caribbean Sea (Haddad and Droxler, 1996), off-shore Somalia (Klöcker and Henrich, 2006; Klöcker et al., 2006) and in the South China Sea (Wang et al., 1997). In the cores from the South China Sea and the Caribbean Sea, the concentrations at ∼20 000 years BP and 150 000 years BP are both recorded, clearly demonstrating that this enhanced

preservation of aragonitic fossils is of global significance and not the result of local variations in water chemistry (Peterson and Cofer-Shabica, 1987; Peterson, 1990, Broecker and Clark, 2002; Sepulcre et al., 2009). Elsewhere in the CAR-MON 2 core, reduced shell calcification occurs during interglacial periods and is particularly poor during extreme stages, such as at MIS 5.5. In the Gulf of Aden (Core KL15), Almogi-Labin et al. (2000) record the near absence of pteropods during interglacials (MIS 13, 11, 9, 7, 5 and 1). The record from this core shows that pteropod maxima appear to be at the glacial/interglacial terminations (especially the MIS 6 to MIS 5 transition). Such deglaciation "spikes" have also been noted by Frenzel (1975) and Berger (1977, 1990). Berger (1977) describes this world-wide phenomenon as a pteropod-rich layer present at the end of the last glacial, although, the exact timing and cause of this event are in some dispute. Serre-Bachet and Guiot (1987) also linked pteropod preservation to colder periods. This link is particularly striking in the post–MIS 2 records in the N.E. Atlantic Ocean (Ganssen et al., 1991), Equatorial Atlantic Ocean (Kassens and Sarntheim, 1989) and the N.W. Indian Ocean (Klöcker et al., 2006). This preservation relationship to colder periods is, almost certainly, due to fluctuations in pCO_2 causing higher pH and increased availability of carbonate during glaciations (Sanyal et al., 1995; Ruddiman, 2001; Hönisch and Hemming, 2005; Yu et al., 2007) and lower pH and reduced availability of carbonate during interglacials. In the CAR-MON 2 data there are some unexpected excursions from the general trend, which show that variations in calcification are not directly proportional to the $\delta^{18}O$ signal. This can be seen particularly between MIS 5.1 and 5.5, where changes in calcification appear to be accentuated.

Several factors during the sedimentation process, which are summarised in Fig. 4, may have influenced the LDX calcification profile. The pattern produced by the LDX profile could not, however, be an artefact of sea floor dissolution and diagenesis. If pteropods within CAR-MON 2 showed a general trend from LDX 0–2 in the near–surface sediments to LDX 4–5 at depth, this would clearly be a diagenetic signal, however, this is not the case. Klöcker et al. (2006) have also noted that, in their core 905 from the N.W. Indian Ocean, diagenesis has had minimal effect on the LDX record. The correlation of pteropod abundances in MIS 2 and MIS 6 across a range of oceans and environments also implies that the LDX profile is caused by global atmospheric CO_2 fluctuations and not merely by variations in local water chemistry.

Water chemistry around the Lesser Antilles island arc is however, complicated by influences of several water masses flowing between the islands and through a number of deeper passages into the Caribbean Sea (Peterson and Cofer-Shabica, 1987; Peterson, 1990, Broecker and Clark, 2002; Sepulcre et al., 2009). Gerhardt and Henrich (2001) found that the influence of Antarctic Intermediate Water (AAIW), towards the south of the island arc, caused moderate to very poor preservation of *Limacina inflata*. However,

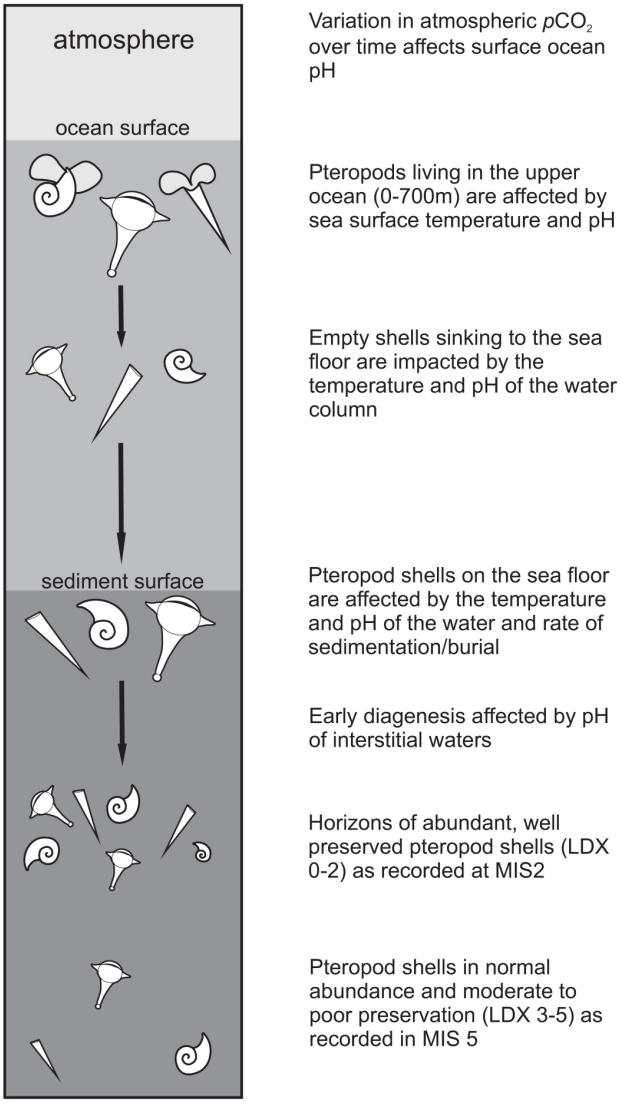

Fig. 4. Conceptualization of pteropod sedimentation, taphonomy and preservation for areas of the sea floor above the aragonite lysocline and aragonite compensation depth. Preservation of pteropod shells is, potentially, impacted by water chemistry during life, passage through the water column (probably minimal as they have quite high settling rates of 1–2.5 cm s^{-1}; see Byrne et al., 1984), on the water/sediment surface and during burial.

towards the north of the island arc, the influence of AAIW is minor due to a large volume of Upper North Atlantic Deep Water (UNADW), which flows through the nearby Anegada Passage. This area consequently shows very good preservation of *Limacina inflata*. Gerhardt and Henrich (2001) place the aragonite saturation depth at 2000 m and the Aragonite Compensation Depth (ACD) at 3800 m water depth in this area. CAR–MON 2 was collected in 1102 m water depth, which is above the aragonite lysocline and ACD, thus discounting any effects that this may cause. It is

also important to note that firstly, no changes in the benthic foraminiferal community were found during our microfossil analysis. This indicates that water masses are unlikely to have changed during the period covered by CAR-MON 2. Secondly, within CAR-MON 2, interglacial periods coincide with a reduced abundance of large (>500 µm) pteropod and heteropod shells (Fig. 3). If the LDX variations seen throughout CAR-MON 2 were due to post-depositional dissolution, a preferential dissolution of small shells would be expected (Lalli and Gilmer, 1989). However, whilst a reduction in the abundance of small shells during interglacial periods was found, there is also a relatively equal reduction in the number of large shells. This suggests a reduction of calcification, rather than an artefact of dissolution. It can therefore be assumed that the variations in pteropod calcification throughout CAR-MON 2 reflect carbonate availability in the surface ocean. A possible interference in the calcification profile may be caused by inputs of volcanic ash, which can reduce the oceanic pH in the local area dramatically during and just after an eruption. A recent study has shown that, under laboratory conditions, volcanic materials entering sea water produce a significant reduction in pH (Jones and Gislason, 2008), reducing the availability of carbonate. This local impact on the pteropod fauna has been investigated and described elsewhere (Jones et al., 2009; Wall-Palmer et al., 2011). However, our observations suggest that, in this case, the ash from the South Soufrière Hills volcano has had little or no effect upon the overall LDX profile. This is because the ash found within CAR-MON 2 is the result of several relatively short-lived events rather than one large, long–lasting event. Ash from these individual eruptions would have been so greatly diluted upon entering the ocean, that the acidic impact upon surface water fauna would have been insignificant. The assumption that the LDX profile is the result of changing carbonate availability is in agreement with recent laboratory work on living pteropods (Fabry et al., 2008; Comeau et al., 2009, 2010a, b) and pteropods from sediment traps in the Southern Ocean (Roberts et al., 2008). It also compares favourably with shell-weight data of *Globigerina bulloides* and *Globigerinoides ruber* provided by recent work in the Southern Ocean (Barker and Elderfield, 2002), in the Arabian Sea (Moel et al., 2009) and in the North Atlantic (Moy et al., 2009).

Our results suggest that the distribution and abundance of shelled pteropod and heteropod fauna, and the quality of their calcification through the last 250 000 years, reflect changes caused by climate variations. This signal appears to be worldwide and may help to predict future changes in the aragonitic holoplanktic fauna caused by increases in pCO_2 and the resulting changes in oceanic pH. However, since the level of anthropogenic CO_2 entering the oceans is now increasing at a rate 100 times faster than any changes seen in the past 650 000 years (Fabry et al., 2008), it might be inappropriate to apply such a model to the modern oceans. The fate of the modern-day aragonitic holoplankton is uncertain, however, this study shows that, at oceanic pH levels relatively higher than those predicted for the 21st Century, euthecosome pteropods have been noticeably affected.

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